Thermodynamic Principles in the Liquid-Phase Reduction of Oxides in an Oxygen Converter

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Researchers are very interested in new energy-saving production technologies.

As we know, metallurgy has been slow to replace existing technologies with more efficient alternatives. Currently, the positive prospects for converter technology are linked to the energy savings associated with the processing of industrial wastes and iron ore by liquid-phase reduction. However, various problems are encountered here. The study of converter processes is most efficiently based on high-temperature and mathematical simulation. Simulation avoids the high cost of trial and error, a method that has been much used in metallurgy. Mathematical simulation permits ongoing selection of optimal parameters in the course of the process. In some cases, new aspects of the converter process may be discovered by such simulation.

In recent years, new approaches to steel smelting have been developed, on the basis of liquid-phase reduction [1, 2] and the direct alloying of steel from iron- and manganese-bearing oxide materials in a smelter or ladle [3]. Researchers are focusing attention on the thermodynamics and kinetics between liquid oxides and various reducing agents. Of particular interest as a reducing agent is solid carbon, which is a relatively accessible fuel. The efficiency of solid fuel in a double role as both a fuel and a reducing agent largely depends on the kinetics of its oxidation or combustion, whether incomplete (to carbon monoxide CO) or complete (to carbon dioxide CO_2). Solid carbon plays a special role, since the reduction of metal from manganese oxide MnO without carbon (in the presence of carbon monoxide or hydrogen) is thermodynamically impossible, while the reduction of iron from ferrous oxide is difficult. Therefore, even for partial reduction of manganese and its transfer to the metal melt, solid carbon must only undergo partial combustion; the nonoxidized carbon residue must be thermodynamically capable of reducing the manganese. Special organization of the process is required to organize this in practice [4].

In the oxygen converter, the reduction and oxidation processes must be divided in time and space (with a reductive period and an oxidative or basic period) [4].

Rational conditions of melt injection with the supply of solid carbon-bearing reducing agents are of interest. It is extremely important here to organize calm injection, with controlled foaming of the slag and without splashing of slag–metal emulsion. Directed circulational flows in the bath ensure bulk interaction of the added iron- and manganese-bearing materials with reducing agent, while effective combustion of the waste gases within the converter and heat transfer directly to the melt compensate for the heat consumption in endothermal liquid-phase reduction of the oxides.

Difficulties arise in general thermodynamic analysis of the multicomponent multiphase system, which is subject to constant external perturbations. It is necessary to identify the basic parameters capable of significantly displacing the system from global equilibrium (with respect to all the phases and components) and markedly changing the means of attaining such equilibrium.

In the present work, we consider a complex metal–slag–gas system, corresponding to the composition of phases in the oxygen converter during steel production. Purely physicochemical phenomena are analyzed. Note that the goals of the process are determined by the technological functions: the removal (oxidation) of metal impurities; and maximum reduction of the iron and manganese from the slag.

The physical interaction mechanism of the phases and components reduces to the following. When they act on liquid metal (hot metal, steel), jets of oxidative gas (especially industrially pure oxygen in an oxygen converter) produce large quantities of iron oxides, which are transferred to the liquid slag phase. With the oxide fluxes typical of the oxygen-converter process, each metal component i (Fe, C, Si, P, Mn, etc.) in the contact zone with the gas phase is oxidized at a rate practically proportional to the mole fraction X_i of this component [5]. Even at the beginning of the process, $X_{Fe} \geq 0.8$ in hot metal. Therefore, iron oxides are formed predominantly in the contact zone of the oxidative gas and the liquid metal. Chemical analysis of the oxide samples during smelting, in both high-temperature models and industrial converters [2, 6], shows that the content of iron oxides in the slag phase is markedly less than expected, especially during the intense oxidation of silicon (at large concentrations in the hot metal)

and carbon. This indicates the reduction of iron from its oxides. In a classical oxygen converter, the reducing agents are silicon, carbon and, in some conditions (as shown by thermodynamic analysis), even phosphorus.

Depending on the reducing agent and the phase parameters of the system and also on the external parameters, the content of iron oxides in the slag may vary over a broad range. The current content of iron oxides in the slag not only determines the development of the basic physicochemical processes but also the economics of the process, as we know [7].

The second important component of the slag phase, whose reduction is of great significance, is manganese monoxide. Even in the highly oxidizing environment of the oxygen converter, manganese is reduced from its higher oxides not only by silicon but by carbon dissolved in the metal. However, manganese may only be reduced from its lowest oxide by silicon, at relatively high concentrations. Nevertheless, taking account of the fluctuations of the components from their standard state, we may select certain conditions for at least partial reduction of manganese from its monoxide in the slag.

In the converter, the reduction of iron and manganese from their lower oxides occurs simultaneously with specified parameters of the system, under the action of the same external perturbations. Therefore, combined thermodynamic analysis of these processes makes sense. In the analysis, we assume that there are special external perturbations; we consider only the classical parameters: the charging parameters (the ratio of the initial materials), the height of tuyere immersion, and the injection rate. Special external perturbations would include preheating of the batch or individual elements of the system (the housing, tuyere, lining, etc.); the use of solid reducing agents (heat carriers); and the addition of iron- and/or manganese-bearing oxide materials.

The present work is based on simulation by thermal analysis of the basic liquid-phase reduction of elements in the liquid metal–liquid–slag–gas system. This method may be used very effectively in developing new technologies and finding alternative batch materials for steel production.

For all the characteristic smelting temperatures, we calculate the basic thermodynamic function of reduction: the standard change $\Delta_r G_i^0$ in Gibbs energy. We consider all the stable iron and manganese oxides at that temperature: Fe_2O_3, Fe_3O_4, FeO and MnO_2, Mn_2O_3, Mn_3O_4, MnO.

All the potential reducing agents are divided into three groups: traditional reducing agents (products of incomplete reaction of solid carbon and natural gas with oxygen: CO, H_2, and solid carbon C_{gr}); impurities in the hot metal ([C], [Si], [P], and even [Fe] for manganese); and reducing elements (C_{gr}, Si, Mn, Al, Ca). Such division into groups is justified. In fact, reactions

with traditional reducing agents have been considerably studied. Reducing elements ensure practically complete reduction of iron and manganese oxides (even FeO and MnO, which are hard to reduce). Impurities in the hot metal offer a unique possibility of combining the removal of harmful phosphorus and the reduction of FeO, say.

Analysis of $\Delta_r G_i^0$ for all the temperatures typical of steel production permits the selection of the most effective reducing agents in different smelting periods. The thermodynamic dependences of $\Delta_r G_i^0$ for the reduction of FeO and MnO by reducing agents from the three groups are obtained from tabular data.

Of the traditional reducing agents (solid carbon, CO, H_2), only solid carbon is able to reduce monoxides of iron and manganese to the metallic state. The reduction of MnO is only possible at $T \geq 1670$ K (around 1400°C). Impurities dissolved in the hot metal (carbon, silicon, and phosphorus) also exhibit reducing properties with respect to FeO and MnO. Silicon is theoretically able to reduce not only FeO but also MnO, which is more difficult to reduce. Reduction of MnO by phosphorus is impossible; reduction of FeO is possible, but only at $T \leq 1547$ K (1274°C). Iron is theoretically able to reduce all the oxides of manganese except MnO. All the reducing elements dissolved in the hot metal (Si, Ca, Al) are able to reduce iron and manganese oxides to the metallic state. The reduction of lower oxides of iron and manganese to the metallic state by solid carbon, with the formation of CO_2 by nontraditional reactions, is only possible at or above 963.5 K and 2401.0 K, respectively.

The thermodynamic potential for individual or combined reduction of iron and manganese irons warrants detailed analysis. In selecting the best reducing agents, account must be taken of technological aspects of the process, the physicochemical expediency of the corresponding reactions, and economic and labor considerations.

The second group of reducing agents (hot-metal impurities) is of primary interest. Maximum use of these extraneous (or even harmful) impurities to reduce iron and manganese oxides is very appealing. Iron (in a practically pure state) is present in the bath throughout almost all of smelting and ladle refining of the steel. Considerable quantities of carbon monoxide are present in the gas phase for most of the smelting period. Expensive and scarce reducing elements should be regarded as reducing agents (especially for higher oxides of iron and manganese) only as a last resort.

CONCLUSIONS

Carbon monoxide cannot reduce even FeO. Solid carbon is able to reduce both FeO and MnO at $T \geq$ 1673 K (1400°C) with negative change in Gibbs energy. With increase in bath temperature to 1400°C or

more, the addition of iron- and manganese-bearing oxide material together with solid carbon may be regarded. The reduction of FeO is possible not only by carbon and silicon but also by phosphorus at $T \leq$ 1547 K (1274°C). Thus, at the beginning of steel smelting, there is theoretically a unique possibility (in the appropriate kinetic conditions) of reducing FeO by removing phosphorus (a harmful impurity) from the hot metal at 1100–1400 K. At 1200–1300 K, the probability of reduction of FeO by carbon and phosphorus is very different from the probability of the reduction of MnO by silicon. The higher oxides of iron and manganese may be reduced by the reaction products of natural gas (carbon monoxide and hydrogen). Therefore, we may recommend the addition of a certain quantity of iron- and manganese-bearing oxide materials to the charge, with simultaneous gas–oxygen injection from the very beginning of the process and the addition of solid carbon when the bath temperature exceeds 1400°C (1670 K).

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